ABSTRACT

In order to decrease both energy consumption and CO₂ emissions, the automotive, aeronautics and aerospace industries aim at making lighter vehicles. To achieve this, composite materials provide good opportunities, ensuring high material properties and free definition of geometry. As an example, for cold applications, the use of carbon fiber/thermoset composites is ever increasing, in spite of a high fiber price. But in a global and eco-friendly approach, the major limitation for their use remains their potential recyclability. Recycling a composite means having a recycling technology available, getting a dismantle solution and an access for the product, and disposing identification plus selection possibilities to the materials. Thus, carbon fibers recovery (i.e. recycling and re-processing) would both help design engineers to balance energy efficiency and cost, and open new opportunities for developing second-life composites, dedicated to the manufacture of medium or low loaded parts (non-structural in many cases).

A first section presents an overview of composite recycling possibilities. Indeed, environmentally and economically, composite incineration is not attractive (even with an energetic valorization), let-alone burying. Reuse and recycling thus remain the two most interesting options.

Aeronautics offers a high potential in terms of fiber deposit. In southwest France, composites recycling will increase in terms of quantity due to dismantling platforms TARMAC (dedicated to civil aircraft applications) and P2P (for the disassembly of ballistic weapons). In addition, from a technical point of view, and even if end-of-life solutions for composites still remain under development, solvolysis (i.e. water under supercritical conditions) already offers the opportunity to recover carbon fibers. The resulting recyclate retains up to 90 percent of the fiber’s mechanical properties.

A second part will explore the recycling to design issue (i.e. how recycling processes have to balance the previous aspects of the end-of-life proposal).

The recycler clearly becomes a new supplier in the carbon fiber lifecycle, by revalorizing wastes with alternatives to burning. Moreover, increasing carbon fiber shelf life reduces its product life impact. Finally, promoting carbon fiber end-of-life would ensure to link aeronautics, automotive, and leisure and sports industries; but one can create demand for recycled reinforcement, by packaging it in useful and attractive forms for those end-users (e.g. pseudo-continuous fiber, felt, strips, bands, patches, etc.).

These sections will be enlightened by several examples from collaborations between I2M and local industries.

NOMENCLATURE

1G : first generation material
2G : second generation material
INTRODUCTION

In the present context of sustainable development, where the anthropic impacts on the environment and the finitude of fossil and mineral resources must be taken into account, manufacturers aim to promote and develop both production fields and products. Composites, that provide good opportunities for combining high modulus materials with free definition of geometry, are no exception. Among them, carbon fiber reinforced composites (CFRCs) (1) and more specially thermoset matrix based composites are currently used by the aerospace, aeronautics and automotive industries, for cold applications. They also become more and more used in the leisure and sports field.

High-tech industries are very strict on the quality of materials, and few already integrate recycled material, even without loss of technical properties (e.g. recycled aluminum). On the contrary, industries involving a wider audience in leisure and sports field may include these recycled materials in order to make it a selling point.

In addition, regulations are steadily increasing the recycling rate to be achieved by products. It becomes necessary to take into account the end-of-life (EoL) of carbon fiber/thermoset composites by (i) avoiding landfill or energy recovery (i.e. incineration), and (ii) exploring the carbon fiber recovery via new stakeholders in leisure and sports fields.

In this paper, we will first focus on the recycling of CFRCs, with a particular attention on the current limitations and legislation in force and those to come. We will see that up today, the recycling of CFRCs especially concerns the fiber itself. In the second part, we will study the possibilities of recovery and the improvement expected for the recycling of CFRCs. Lastly, two examples of integration of recycled fibers in sport products will be shown.

THE RECYCLING OF CFRCs

Legislation in force for composites

Composites are not differentiated within legislation. Their EoL is indirectly involved in the waste electrical and electronic equipment directive (WEEE) (2) and in the legislation for landfill of wastes (3). Composites are also mentioned in the REACH legislation (Registration, evaluation, authorization and restriction of chemicals) (4) as soon as they contain some toxic or harmful substances such as flame-retardants, currently used in aeronautics.

Only the legislations on end-of-life vehicles (ELVs) mention composites recycling. Indeed, the rate of reuse and recovery should reach 95% in 2015, and 85% for reuse and recycling, in average weight per vehicle and per year, according to the European directive “VHU 2000/53” (5).

European directives about WEEE and end-of-life thus force industries to seek new methods of recovery for composite parts. In this context, composites recycling will increase in terms of quantity due to the creation of dismantling platforms. As local examples, in southwest France, the TARMAC platform (acronym for Tarbes advanced recycling & maintenance aircraft Company) is dedicated to civil aircraft applications in collaboration with EADS-Airbus and EADS-Sogerma. They mainly focus on reuse and certification of replacement parts in aircraft maintenance. Also, the P2P platform (in the Bordeaux area) deals with the disassembly of ballistic weapons.

Thereafter, we will especially focus on carbon fiber (e.g. ex-PAN T800, T300, etc.) and thermoset matrix (e.g. epoxy) based composites, currently used by aeronautics and aerospace industries (e.g. Safran-Snecma Propulsion Solide, EADS Astrium Space Transportation, etc.). Lastly, one must notice that several types of materials are concerned (involving raw materials: RM), from unused fiber or pre-pregs, to composite offcuts and life-ending composites.

Assessment of CFRC recycling

A deeper study of the composites end-of-life is really needed. Landfill and energetic valorization are the oldest options for composites EoL. Knowing that CFRCs are made with non-renewable materials and that they are quite expensive (e.g. carbon pre-preg: approx. 180 €-kg\(^{-1}\)), giving them a new life by recycling is a better option both economically and environmentally. Recycling a composite means having a recycling technology available, getting a dismantle solution and an access for the product, and disposing identification plus selection possibilities to the materials. Thus, carbon fibers recovery (i.e. recycling and re-processing) would both help design engineers to balance energy efficiency and cost, and open new opportunities for developing second-life composites, dedicated to the manufacture of medium or low loaded parts (non-structural in many cases).

Several techniques exist in order to recycle CFRCs (6), (7):
- Mechanical recycling consists in grinding fiber and matrix. This technique makes no distinction between composites containing varying ratios of matrix and fibers. It’s cheap but very aggressive for the carbon fibers (8, 9), as it requires the destruction into simpler components used in various sectors. The ground material is reincorporated as filler (powder) or used in a chopped strand mat (short fibers). A last option consists in their use as a mineral phase in concrete. The mechanical recycling consists merely in a material valorization.

- The thermic recycling can be led by oxidation in fluidized bed, by pyrolysis, or by treatment in molten salt bath (10). Pyrolysis is the technique that is the more used at the present time.

- The chemical recycling (based on the matrix solvolysis by water under supercritical conditions) includes all methods of cold recycling (temperature lower than 450°C, and pressure around 250 bar, depending on the matrix polymerization degree), with the use of chemicals (10).

  Each technique presents advantages and drawbacks (Table 1) (10). But the main limitation for the use of recycled CFRCs (rCFRCs) remains in the fiber length. In this way, rCFRCs are mainly used as ground material forms in the building and civil engineering (11). They are also integrated in non-structural parts (e.g. as filler) in the automotive industry. But obviously, the main advantage of a reinforcement recovery is then completely lost. On the other hand, the chemical method gives the opportunity to recover quite long carbon fibers and to preserve mechanical properties. The fiber length thus directly depends on both size of the to-recycle piece (unused pre-preg, offcut or used composite) and dimension of the solvolysis reactor (12). Furthermore, the resulting recylcate retains up to 90 percent of the fiber’s mechanical properties. In some cases, the method enhances the electrical properties of the carbon recylcate because the latter can deliver a performance close or superior to the initial material (13). Nevertheless, the economic viability of the chemical recycling solution including chemical processes has yet to be demonstrated and validated on an industrial scale (11).

  In such cases, second use of composite fibers will be dedicated to the manufacture of medium or low-loaded parts (non-structural in many cases). Indeed, the recycled fibers and reprocessed semi-products must reach the full acceptance and the trust of users, i.e. designers, who are not already keen on integrating rCFRCs when high mechanical properties are needed (e.g. in high-tech industries). Nevertheless, foreseen markets exist: automotive (in semi-structural parts) (Table 2) and leisure and sports industries (10). For all these reasons, it is necessary to improve the carbon fibers recycling processes and to create demand for rCFRCs, by packaging them in a form useful or attractive to end-users. For example, cheap materials with very good properties could find larger applications than composites today. Moreover, these materials, resulting from a reprocessing path, are more environmental-friendly, and possess the potential of a new recycling loop.

Towards a CFRCs partial recycling choice: design of a recycling line for carbon fibers

The Mechanics Institute of Bordeaux (I2M Bordeaux) was involved in the RECCO projects (acronym for Recycling carbon fiber reinforced composites) alongside a consortium of rocket manufacturers (EADS-Astrium Space Transportation, Safran-Snecma Propulsion Solide, etc.) in order to manage the end of life of composite structures. The final goal was to validate an industrial solution and an industrial demonstrator for composite recycling. The solvolysis process has been chosen for removing the thermoset matrix. Thanks to this, the lifecycle of the carbon fibers is extended by the CF regeneration that allows the cycle to be closed (Figure 1).

Let’s focus on the fiber carbon life. The first generation (1G) composite is made by the association of new carbon reinforcement (1G CF) and an epoxy matrix. At the composite end-of-life, the solvolysis process leads to the fiber recovery. It may be noticed that today, matrix is lost, but it can be recovered in a parallel process in order to provide heat for another solvolysis. The recovered fiber (2G CF) can thus be used to process a second composite (2G composite).

Assuming the absolute recyclability of the fiber, this representation can be generalized to an nG carbon fiber. Thus, the composite based on this reinforcement will be called nG composite.

In reality today, product lifecycles from different industries are not connected and the carbon reinforcement is at best promise to an energetic valorization (dotted line on Figure 2). Considering the aeronautics, automotive and leisure and sports industries, products lifecycles work in closed system (i.e. there are no interactions between them), but not necessarily in closed lifecycle (maybe except for the automotive industry that allows the use of ground composites). We propose to link these three industries by improving CFRC’s end-of-life. As soon as an industry does accept rCFRCs from another one, they are linked together. Specialists of the EoL have opportunities to improve a material usually non upgradable in a new potential source of raw material.

Taking into account the limitations previously listed (length of the recovered fiber, designers’ reluctances, etc.), the complete CF lifecycle can be drawn as in Figure 2 diagram. It is a cylindrical representation of the successive integrations of the (recycled) CF in different product lifecycles. Only the main steps of each lifecycle are displayed:

- integration of the raw materials (in particular carbon reinforcement);
- design, process and production of the composite;
- product distribution and transport;
- use and maintenance;
- and product end-of-life.
### Process Advantages Drawbacks

#### Mechanical
- Recovery of both fibers and resin
- No use or production of hazardous materials
- Significant degradation of mechanical properties
- Unstructured, coarse and non-consistent fiber architecture
- Limited possibilities for re-manufacturing

#### Pyrolysis
- High retention of mechanical properties
- Potential to recover chemical feedstock from the resin
- Possible deposition of char on fiber surface
- Strength degradation between 25% and 50%
- Fiber length degradation
- Unstructured (“fluffy”) fiber architecture
- Impossibility for material-recovery from resin
- Limited possibilities for re-manufacturing

#### Fluidized bed
- High tolerance to contamination
- No presence of residual char on fiber surface
- Well established and documented process
- Strength degradation between 25% and 50%
- Fiber length degradation
- Unstructured (“fluffy”) fiber architecture
- Impossibility for material-recovery from resin
- Limited possibilities for re-manufacturing

#### Chemical
- Very high retention of mechanical properties and fiber length
- High potential for material-recovery from resin
- Common reduced adhesion to polymeric resins
- Low contamination tolerance
- Reduced scalability of most methods
- Possible environmental impact if hazardous solvents are used

### Table 1. Summary analysis of different recycling processes (quote from the table by Pimenta et al. (10))

<table>
<thead>
<tr>
<th>Type of rCFRC</th>
<th>Possible processes</th>
<th>Foreseen markets for rCFRC</th>
<th>Examples of current solutions with virgin materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-reinforced</td>
<td>Pyrolysis, Fluidized bed, Chemical</td>
<td>BMC compression, Compression molding of non-woven mats</td>
<td>Automotive semi-structural parts, Equipment housing</td>
</tr>
<tr>
<td>Medium reinforced</td>
<td>Pyrolysis, Fluidized bed, Chemical</td>
<td>Compression molding of non-woven mats</td>
<td>Automotive non-critical structures, Aircraft interiors</td>
</tr>
<tr>
<td>Aligned</td>
<td>Pyrolysis, Chemical</td>
<td>Compression molding of aligned mats, Lay-up of aligned pre-pregs</td>
<td>Automotive non-critical structures, Aircraft interiors, Wind turbine non-critical structures</td>
</tr>
<tr>
<td>Woven</td>
<td>Pyrolysis (pre-preg rolls), Resin infusion, RTM</td>
<td></td>
<td>Automotive structures, Wind-turbine structures</td>
</tr>
</tbody>
</table>

### Table 2. Potential structural applications for rCF/thermoset matrix composites (quote from the table by Pimenta et al. (10))

### Figure 1. Lifecycle of a CFRC, from resources to the carbon fiber regeneration
The ordinate of each lifecycle depends on the level of specifications (i.e., number of constraints) of the composite. Three examples are chosen \( (n \in [1;3]) \), assuming integrations in, first, aeronautics, then automotive, and finally leisure and sports industries. It might be noticed that, even if leisure and sports industry has been placed under automotive, it might be at the same ordinate regarding level of use constraints.

The radius \( r \) of each cycle is linked to the number of potential uses for the (r)CF, i.e., particularly to the fiber length (or the nature of the semi-product) and its mechanical properties. Lastly, the angle \( \theta \) represents time modulo the \( n^{th} \) cycle duration.

Based on this lifecycle and on the team expertise, each recycling step can be detailed and a recycling line for carbon fiber can been designed. An arborescent representation detailing possible processes is given in Figure 3. The \( nG \) product is

- sorted. Indeed, it is impossible to recycle different types of matrix simultaneously; moreover, specific coatings like metallic cladding for electric behavior, are also not compatible with some recycling processes;
- dismantled (all metallic insert have to be extracted) and cut (i.e., adapted to the recycling process reactor);
- and, lastly, solvolysed.

Thus, the carbon fabric is unwoven. I2M has developed a prototype device for this purpose. The fibers are hackled, possibly mixed (depending on available CFs, or on the quality of the chosen reinforcement for the \( (n + 1)G \) material), and reinforced to be integrated more easily in the next recycling stage (e.g., prepreg). Depending on the \( (n + 1)G \) composite elaboration process (RTM, infusion, etc.), fibers can be spun, then rewoven or knit, or made available as prepreg strips, to finally process the composite.
The interactions between stakeholders and the associated quality criteria will be developed below.

DEVELOPMENT OF A CFRC RECYCLING NETWORK

Development of a CFRC recycling network is needed. First, we face a growth in deposit that cannot be kept nor incinerated. Moreover, CFRCs are expensive; used CFRCs could be a valuable resource by being recycled. Getting a
longer fiber allows more potential uses in a new life. We will focus on this thematic.

In order to improve the carbon fibers end-of-life, we propose a methodology based on those stages:
1. Definition of the requirements;
2. Identification of the actors;
3. Identification of possible interactions between stakeholders.

**Definition of the requirements**
As widely discussed above, the main objective is to develop a viable recycling line for CFRCs. It will be based on a recycling process that allows longer CFs to be recovered. We now explore opportunities to improve the fiber end-of-life.

**Identification of the actors for the recycling line**
Protagonists of the CFRC recycling network can be clearly identified (Figure 4). The suppliers are the manufacturers of the 1G carbon fiber and the epoxy matrix. The three main designers of these supplies are the aeronautics, automotive and leisure and sports industries. Customers should be either industrialists or individuals. Specialists of the EoL are pullers, dismantlers and recyclers (possibly the same actors).

![Figure 4. Actors of the CFRC recycling network](image)

**Identification of possible interactions between the actors**
The Figure 5 corresponds to the Figure 2 seen from above. The lifecycles of each of the three industries are linked by an exchange of carbon fibers at the end-of-life stage. The stakeholders (suppliers, designers, customers and recyclers) and their interactions are highlighted (a summary is given in Table 3).
- Suppliers adapt their offer from the designer’s needs (market research). They should also be related to recyclers who have to take into account the specifications and cost of the raw materials.
- Designers are getting information from customers with market research; they choose suppliers according to raw materials specifications and cost.
- Customers decide to buy or not the product, according to multicriteria decisions; they are related to recyclers by legislation (for industrials) or thanks to environmental awareness (for individuals).
- Recyclers are those collecting used CFRCs, whose deposit must be taken into account, as it is becoming stable in terms of source of supply. They then become the new suppliers in the carbon fiber lifecycle, by revalorizing wastes with alternatives to burning. They choose the appropriate recycling process in order to propose a material adapted to the (n+1) designer’s needs.

We now aim at focusing on links between customers and recyclers. A sorting and collection network has to be developed to feed a recycling line at an industrial scale. It is important that the network be placed in a local or regional area. Indeed, industrials are no more the only ones getting involved in the cycle; leisure and sports customers can take place without too much effort. By developing a local network, the problem usually raised by collection will be avoided.

At the same time, we hope to promote discussion between designers and recyclers in order to innovate in the definition of new recycled composite products. This means that information and skills from both sectors will be shared. However, it also implies that materials and mechanical knowledge have to be developed for both designers and recyclers. Therefore, it is necessary to include a third party in the discussion: experts in material and mechanical characterization.

Lastly, in the carbon fiber recycling line, discussions between stakeholders must be improved by defining semi-products specifications and formalizing those interactions by quality criteria (dotted lines in Figure 3). The latters are based on the processes efficiency.

**Examples of applications.**
**Demonstrators processed in the Mechanics Institute of Bordeaux (I2M Bordeaux)**
It is possible to develop specific markets that would use recycled carbon fibers, even if they are marginal. Leisure and sports certainly propose the most important niche markets that could make the use of rCFRCs more effective. Two examples are chosen among the demonstrators processed at the Mechanics Institute of Bordeaux, within the context of the RECCO projects (37).
Figure 5. Figure 2 seen from above. Highlight of the stakeholders (suppliers, designers, customers and recyclers) and their interactions.
Note that the recyclers become new suppliers in the CF lifecycle.

<table>
<thead>
<tr>
<th>Suppliers</th>
<th>Designers</th>
<th>Customers</th>
<th>Recyclers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suppliers</td>
<td></td>
<td>Specifications</td>
<td>Market research</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cost</td>
<td></td>
</tr>
<tr>
<td>Designers</td>
<td>Market research</td>
<td>n/a</td>
<td>Purchase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Multicriteria</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>choice</td>
</tr>
<tr>
<td>Customers</td>
<td></td>
<td>Collection</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Market research</td>
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</tr>
<tr>
<td></td>
<td>Cost</td>
<td>Cost</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Legislation (industries)</td>
<td>Environmental awareness</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Interactions between stakeholders (∅: no interaction).
(Interactions to be developed are set in bold and italic type)

Rooryck has created a startup focused on high quality composite products for the equestrian field. He wanted his company and its products to stand out from the competition with larger groups, integrating a strong sense of respect for the environment. The use of recycled carbon fiber presented a great opportunity to meet this goal. An equestrian gaiter that protects horses’ tendons (Figure 6) has been processed. The same mass (approx. 130 g) and a stiffness equivalent to the mass-market gaiters have been reached. The appearance of the 2G gaiter is very different from the mass-product one but very attractive, because of its uniqueness.
We now have the hope to attract the interest of designers of composite visible parts that may include a low-cost carbon fiber with a unique aspect. Moreover, as recycled fiber absorbs more matrix than the 1G reinforcement, it creates a sandwich material which gives a greater thickness to the 2G product. Thus, even if the stiffness of the recycled fiber was inferior to that of a 1G CF, the stiffness of the product containing recycled fiber would be increased. This feature allows the use of a smaller amount of recycled carbon fiber for the same product. Thus the use of recycled products for flexibility and/or aspect will certainly prove very economical due to both the low price of the recycled fiber and the possibility of using less material. In addition, contact molding showed no particular difficulty to use realigned 1G CF patches, which validates the processability of using recycled fiber in this process.

To enhance the quality of the recycled carbon fiber, an application has been sought with a more general public target, and submitted to mechanical stresses, with an attractive form and a high-performance product. Natec manufactures one of the lightest racing bike pedal board in the world. A crank has been processed with recycled carbon fibers (Figure 7). It shows a very acceptable aspect. Its mass is 187g versus 163g for the 1G mass-product. It has been shown that the use of recycled fibers was simpler than the use of carbon woven fabric. Finally, no fiber displacement has been observed during the process; this perfectly validates the possibility of using 2G fibers by compression molding.

CONCLUSION AND PERSPECTIVES

The recycling of CFRCs is a quite recent problematic, due to the increase in their use. As a consequence, the legislations in force barely cite composite materials; they are simply mentioned in the WEEE and ELVs directives. As a consequence, both industrialists and individuals have yet to become aware of the usefulness of CFRCs recycling. However, a recycling network, capable of processing the CFRC recycling (and not only an energetic valorization) tends to develop.

We have spotlighted that the improvement of local or regional sorting and dismantling platforms remains necessary. Based on the solvolysis process, the recycling is thus achievable. But a sorting and collection network must be developed to feed the recycling line at an industrial scale. All the stakeholders to involve in this line already exist; we now aim to link them. Promoting discussion between designers and recyclers in order to innovate in the definition of new recycled composite products will induce the creation of exchange platforms, allowing information from both sectors to be shared. However, it also implies that materials and mechanical knowledge have to be developed for both designers and recyclers. Therefore, it is necessary to include a third party in the discussion: experts in material and mechanical characterization. Lastly, promoting carbon fiber end-of-life would reinforce the link between aeronautics, automotive, and leisure and sports industries; but one can create demand for recycled reinforcement, by packaging it in useful and attractive forms for those end-users. Lastly, the leisure and sports industries seem to already propose the most important niche markets that could make the use of rCFRCs to come into effect.

REFERENCES


